



Catalytic activity and long-term stability of palladium oxide catalysts for natural gas combustion: Pd supported on LaMnO₃-ZrO₂

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ARTICLE INFO

Article history:

Received 21 May 2009

Received in revised form 29 July 2009

Accepted 3 August 2009

Available online 7 August 2009

Keywords:

Methane catalytic combustion
Supported Palladium oxide catalysts
LaMnO₃-ZrO₂ catalyst support
SO₂ poisoning
Ageing mechanism

ABSTRACT

The catalytic activity and long-term stability of 2% Pd/LaMnO₃-ZrO₂ catalysts for natural gas combustion were deeply investigated. The catalyst, prepared via solution combustion synthesis, was completely characterized (XRD, BET, FESEM/EDS, TPC/TPD/TPR and FT-IR analysis) in the fresh status, and in the aged one, after prolonged treatment under hydro-thermal ageing and S-compounds poisoning (up to 3 weeks of hydro-thermal treatment at 800 °C under a flow of domestic boiler exhaust gases typical composition of 9% CO₂, 18% H₂O, 2% O₂ in N₂, including 200 ppmv of SO₂). An increased catalytic activity towards NG combustion with ageing was detected: the *T*₅₀, in fact, got lowered from 570 (fresh sample) to 465 °C (after 3 weeks ageing). Highly dispersed Pd centers were predominant on fresh catalyst. Upon ageing, oxygen covered Pd metal particles formed, at the expense of dispersed cationic and zerovalent Pd atoms. The increase in the catalytic activity was associated to the phase modification occurring in the bulk support, where Mn oxides, active towards CH₄ combustion, segregated. Moreover, bands due to sulfate species were detected in aged samples: IR analysis showed that Pd atoms did not interact significantly with these species. The bands of sulfate species decreased in intensity after 3 weeks ageing, likely mostly due to sintering of the catalyst, with the corresponding decrease in the surface area.

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1. Introduction

Palladium based catalysts appear to be the most active catalysts in natural gas combustion [1,2]. Different opinions are reported in literature concerning the nature of the active species for light hydrocarbon combustion. The active phase of Pd oxidation catalysts is mostly identified as palladium oxide [3–8], which is known to decompose into Pd metal in the range 700–850 °C depending on oxygen partial pressure [9,10]. The mechanism of PdO formation and decomposition on supporting oxides in a reaction stream containing both CH₄ and O₂ is a complex one: in some particular conditions [7,11], the specific combustion activity of supported PdO catalysts towards CH₄ combustion showed a persistent hysteresis between 450 and 750 °C, with the rate of combustion in this temperature range strongly depending on whether the catalyst was in the cooling phase from temperature above 750 °C or in the heating one from temperature below 450 °C.

The observed differences in combustion rates at temperatures higher than 450 °C were caused by the extent of formation of surface oxide complexes, which was, in turn, determined by the morphology of bulk Pd metal and oxide phases: the development of active PdO surface is, in fact, significantly temperature dependent as well as time dependent [7]. *In situ* XRD analysis and Raman investigations [11] showed that the formation of PdO crystallites started at around 300 °C, with a very slow and gradual crystallization phase up to 550 °C. The transformation of PdO into Pd is reported to negatively affect catalytic reaction by lowering conversion, CH₄ combustion activity being reversibly restored upon re-oxidation of Pd to PdO. However, these conclusions mostly arise from quite high-loading Pd catalysts. The existence of species different from Pd and PdO massive particles, such as atomically dispersed Pd⁰, Pd⁺, Pd²⁺ and Pd⁴⁺ species, has been proposed on the frame of spectroscopic investigations on low-loading catalysts [12–14]. Additionally, recent surface science studies with innovative techniques performed on model “planar” catalysts [15], as well as theoretical investigations [16], provided additional detailed information on the catalytic oxidation over dispersed Pd catalysts. The most recent results on CH₄ lean combustion seemed to suggest for low-loading Pd-based catalysts [11,17] the primary role of a

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mixed PdO/Pd phase in enhancing CH₄ combustion at a relatively low temperature. In particular, very small Pd metal clusters and Pd oxide species coexist and likely work synergistically: CH₄ activation may be easier on Pd metal, Pd oxide providing O₂ species to form CO₂ [17]. Oxygen, in fact, seems more strongly bound to Pd in small particles than in large ones, likely due to interactions with the support [11].

On the other hand, the support also plays a remarkable effect on both catalytic activity and stability. Alumina is the most largely used support, due to excellent activity [18,19], and stability, but addition of ceria is reported to be beneficial both in terms of activity [20,21] and stability to sulfation [22]. Zirconia [23–25] and ceria-zirconia [17,24–28] supported catalysts were also investigated.

Lanthanum-transition metal perovskites (LaBO₃) received a lot of attention, thanks to their good thermal stability and high activity [29–36], and the corresponding stabilization of unusual oxidation states of the active metal ions in B position [35]. High oxygen mobility observed in many perovskites, in particular for LaBO₃, is generally considered as an additional advantage [32,33,35]. In particular, perovskite LaMnO₃ may contain Mn⁴⁺ (more or less abundant in dependence of the preparation conditions used) in addition to Mn³⁺, exhibiting thus a cationic defectivity in the lattice and, in turns, high reaction activity [36]. The presence of Mn in two oxidation states (Mn³⁺/Mn⁴⁺), resulting in a relatively stable and constant oxygen excess [35], could be the main origin of the high activity of LaMnO₃.

Finally, dispersing a noble metal over a support intrinsically active towards catalytic oxidation, such as Mn-containing perovskites [31,37–40] is expected to have favorable effects on the overall catalytic activity.

Based on these considerations, new catalysts were developed for natural gas combustion in domestic applications, based on Pd/LaMnO₃-ZrO₂ [41–45], trying to improve the overall morphological properties by mixing the perovskite with zirconia. The technique used to synthesize these materials, the solution combustion synthesis (SCS) [32,41,46,47], was particularly suited to obtain high dispersion of the metals and small catalyst particle size.

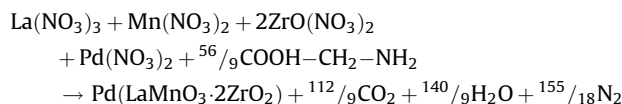
In the present paper, the characterization study of LaMnO₃-ZrO₂ supported 2% Pd catalyst, hereafter named PLZ, developed for premixed natural gas combustion within catalytic porous media, is reported. This system was found to represent an excellent solution for energy production for domestic applications [41–45]. The aim was to investigate the details of the catalytic active sites and its deactivation behavior under severe hydro-thermal ageing and sulfur poisoning conditions. In our previous works [44,45], in fact, the analysis of low-environmental-impact premixed metal fiber burners for natural gas domestic boilers showed that these systems presented a very good performance in terms of reduction of noxious emissions (CO, NO_x), with performance improvement when exposed to severe sulfur hydro-thermal ageing (i.e., further reduction of NO_x and CO, in particular, compared to the burners tested in the fresh status). The conditions used in the present study to simulate the sulfur hydro-thermal ageing of the catalytic powders, in terms of temperature and ageing atmosphere, were the same adopted in the real domestic boilers studied in the past [44,45] as concerns the possible poisoning exhaust compound, but with many folds increased concentration to accelerate the phenomena and see in short ageing time long-term effects.

2. Experimental

2.1. Catalyst preparation

PLZ powdered catalysts were one-shot prepared via SCS, a process based on the oxidation of an organic fuel, like glycine,

which provides the necessary synthesis heat [41,47]. Metal nitrates of La, Mn, ZrO and Pd (Aldrich, 99% purity) were used as precursors, acting as oxidizers of glycine in solution. The organic molecule played a double role: by forming complexes with metal cations in aqueous solution, it guaranteed good solution homogeneity, preventing the preferential precipitation of ionic species, and reacted with the precursors (metal nitrates). The overall combustion reaction can be written as:



The precursors and fuel, dosed in the stoichiometric amount, were dissolved in distilled water and the resulting solution, thoroughly stirred to ensure complete dissolution of all reagents, was then transferred in a ceramic dish and placed into an electric oven set at 450 °C. After water evaporation and a significant increase in the system viscosity, the heat released in the fast reaction allowed the formation of the catalytic powders. Subsequently, the as-prepared powders, after grinding in an agate mortar, were calcined in oven at 800 °C for 2 h in still air [41], so as to both favor the decomposition of the eventually unreacted nitrate precursors and promote the formation of the perovskite structure.

2.2. Sulfur hydro-thermal ageing

Since Pd/oxide-based catalysts are prone to be poisoned by sulfur compounds (normally used as odorants in natural gas networks), the catalytic powders were kept in an electric tubular oven at 800 °C (a thermocouple was used to monitor the furnace temperature) under a flow rate with typical domestic boiler exhaust composition (9% CO₂, 18% H₂O, 2% O₂ in N₂); 200 ppmv of SO₂ were added too [42–44]. The latter value was chosen several times higher than the odorant supplementary concentration in commercial natural gas (about 8 ppmv, in Italy, as tetrahydrothiophene, THT) so as to accelerate any possible poisoning effect [43,48,49]. Earlier sulfur poisoning studies on perovskite catalysts showed that the basic poisoning mechanism under catalytic combustion conditions was chemisorption of SO₂/SO₃ species generated by combustion of whatever sulfur-organic compound present in the feed (e.g. odorants) [48]. Particularly, it was demonstrated that the direct presence of SO₂ or of THT odorant in the feed did not lead to a significantly different ageing effect, provided the overall sulfur content remaining the same. SO₂/SO₃ species, in fact, resulted from the total oxidation of S-containing organics during the combustion process [50]. For this reason only ageing runs with a SO₂-laden flow were accomplished. The catalytic powders were continuously aged up to 3 weeks: for a domestic boiler, such operating time in 200 ppmv SO₂ atmosphere may be considered equivalent to a utilization life time of approximately 3 years under real operation [44]. The as-prepared catalysts were completely characterized at fresh status and after each week of ageing (F/1W/2W/3W samples).

2.3. Catalysts characterization

The crystal phases and grain size of the various catalysts were detected by X-ray diffraction (Philips PW1710 apparatus equipped with a monochromator for the Cu Kα radiation; markers located according the PcpdWin database).

The morphology of the powders was studied using a Scanning Electron Microscope (FESEM Leo 50/50 VP with Gemini column).

The surface area and the pore size distribution of all samples were determined by N₂ adsorption at the liquid N₂ temperature in

a Micrometrics ASAP 2010 M instrument. The surface area was determined according to the Brunauer–Emmett–Teller theory; the samples were degassed in vacuum for at least 4 h at 250 °C before analysis.

Oxygen Temperature Programmed Desorption (O_2 -TPD) and hydrogen Temperature Programmed Reduction (H_2 -TPR) analysis (Thermoquest TPD/R/O 1100 Series, Thermo Finningan analyzer, equipped with a thermal conductivity detector TCD) were employed to investigate the O_2 desorption with temperature and to quantify the presence of PdO on the surface on fresh and aged catalysts. TPR tests were performed on fresh and aged (1W and 3W) catalysts by flowing $10\text{ N cm}^3\text{ min}^{-1}$ of 5% H_2 in Ar, increasing the temperature from 50 to 900 °C at 10 °C min^{-1} and evaluating by TCD the H_2 consumption. To determine the reference global amount of potential PdO (with the assumption that it remained the same for fresh and aged catalysts), firstly a complete oxidation treatment was performed on the fresh catalyst by flowing $40\text{ N cm}^3\text{ min}^{-1}$ of pure O_2 and increasing the temperature from 25 to 750 °C at 40 °C min^{-1} ; the test ended by cooling to room temperature in the same oxidizing atmosphere. Then, TPR tests were performed on both the so completely oxidized PLZ catalyst and the support $\text{LaMnO}_3\cdot\text{ZrO}_2$ (LZ) without noble metal: once again, $10\text{ N cm}^3\text{ min}^{-1}$ of 5% H_2 in Ar flowed through the samples, increasing the temperature from 50 to 900 °C at 10 °C min^{-1} . The reference global amount of potential PdO was calculated as the difference between the integral TCD curve (linked to the adsorbed H_2 volumes) of the completely oxidized PLZ catalyst and that of the LZ support. The PdO oxide percentages on fresh, 1W and 3W PLZ catalysts were calculated considering their integral adsorbed H_2 connected with the TCD curves (reduced by the LZ support effect) related to the reference global amount of potential PdO.

The catalytic activity towards CH_4 oxidation of the fresh and aged catalytic powders was tested in a lab-scale fixed-bed reactor (Temperature Programmed Combustion, CH_4 -TPC). 0.1 g of each as-prepared catalyst was mixed with 0.9 g of SiO_2 (0.2–0.5 mm in size, to prevent the catalytic bed clogging), sandwiched between two quartz wool layers, and inserted in a quartz tube (4 mm ID). The obtained reactor was placed into a PID regulated electrical oven and fed with $50\text{ N cm}^3\text{ min}^{-1}$ of a gaseous mixture containing 2% CH_4 and 16% O_2 in He [41], which corresponded to a gas hourly space velocity (GHSV) of 6000 h^{-1} . The reactor temperature was measured by a K-thermocouple placed inside the catalytic bed. By feeding the reactive gaseous mixture, the catalytic bed was first heated up to 800 °C at 50 °C min^{-1} , then the oven temperature was decreased at 2 °C min^{-1} rate by monitoring the outlet CO_2 , CO, CH_4 and O_2 concentrations with a continuous analyzer (NDIR and paramagnetic Uras 14, ABB), thus allowing to evaluate CH_4 conversion. For each catalytic powder, the measurements were repeated thrice to assess the repeatability of the analysis. The temperature where the 50% of CH_4 conversion was reached (T_{50}), was considered as an index of the powders catalytic activity.

For IR studies, pressed disks of the pure catalysts powders were activated “*in situ*” by using an infrared cell connected to a conventional gas manipulation/outgassing ramp. All catalysts were first submitted to a treatment in air at 400 °C for 30 min, followed by evacuation at the same temperature before the adsorption experiments. In order to obtain the reduced catalysts, after the mentioned evacuation, they were put in contact with a H_2 pressure of $\sim 40\text{ kPa}$ at 400 °C for 30 min, and successively outgassed at the same temperature. CO adsorption was performed at -140 °C by the introduction of a known dose of the gas (1.32 kPa) inside the low temperature infrared cell containing the previously activated wafers. IR spectra were collected, evacuating at increasing temperatures between -140 and 0 °C . Spectra were recorded in the temperature range -140 °C /room temperature by a

Nicolet Nexus FT instrument. For skeletal spectra, KBr pressed disks were used.

3. Results

In Fig. 1 the CH_4 -TPC curves for the fresh and the aged samples are reported. The fresh catalyst started to convert CH_4 near 300 °C while total conversion was obtained near 670 °C. The performance of this fresh catalyst was definitely lower than that of Pd/CeO₂-ZrO₂ catalyst described elsewhere [17], which already converted entirely CH_4 in the same conditions at 450 °C, with detectable conversion already near 250 °C. After a first slight decay in 1W sample, CH_4 conversion was substantially improved with 2 weeks ageing. 3W sample showed slightly lower activity than 2W one. Both 2W and 3W catalysts showed the typical decrease in catalytic activity above 500 °C, followed by a further increase at around 600 °C, which is attributed to the conversion of PdO into Pd metal [1,6,51]. These experimental results were in agreement with some literature data [7,10] where, in conditions similar to ours, the specific combustion activity of PdO supported on Al_2O_3 showed a persistent hysteresis between 450 and 750 °C. The hysteresis in CH_4 combustion rate was caused by higher activation energy for reduction of oxygen chemisorbed on metallic Pd and by suppressed re-oxidation of Pd metal relative to PdO decomposition [7]. In any case, it is worth noting that the definite improvement of the catalyst performance after 2 weeks ageing makes this catalyst definitely better than the above mentioned Pd/CeO₂-ZrO₂ catalyst, previously studied [17], which progressively deactivated upon ageing and was definitely less performing after 2 weeks.

The XRD patterns of the fresh and aged PLZ catalysts are shown in Fig. 2. Weak diffraction peaks of tetragonal ZrO₂ and orthorhombic perovskite LaMnO_3 were detected in F/1W samples. ZrO₂ phase segregated further with ageing. The presence of $\text{La}_2\text{O}_3\cdot\text{SO}_4$, $\text{ZrO}\cdot\text{SO}_4$ and segregated Mn oxides, increasing with the ageing time (2W/3W), was also detected. In literature, perovskites poisoning by SO_2 is sometimes reported to be associated to the formation of sulfate and their amount accumulated at the surface in form of $\text{La}_2(\text{SO}_4)_3$, as well as, to the segregation of simple oxides [52]. XRD did not reveal the presence either of metal Pd or of PdO, sign of the good degree of Pd dispersion on the carrier.

The BET surface area values, reported in Table 1, were very high for the fresh catalyst (strongly related to the synthesis method that allows to process powder with high surface area [32,47]), but decreased significantly upon ageing, in particular after 2 weeks. The crystal size calculated from the XRD pattern was much smaller for ZrO₂ than for LaMnO_3 , a sign that the ZrO₂ surface should be predominant on the support.

The SEM images reported in Fig. 3 showed that the fresh powder was characterized by a spongy structure, perforated waffles with

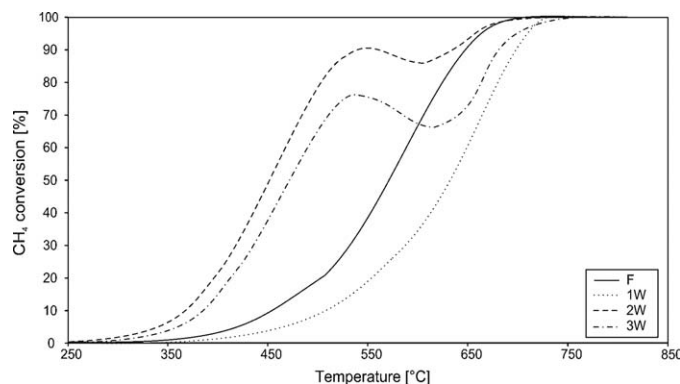


Fig. 1. CH_4 Temperature Programmed Combustion (TPC) curves of the PLZ samples under study.

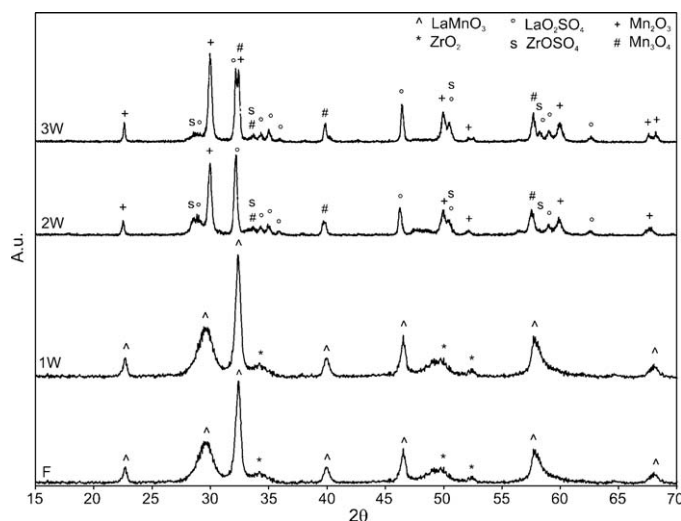


Fig. 2. XRD patterns of the PLZ samples under study.

nanometric pores and complex network configuration. After 1 week of treatment, the morphology changed radically exhibiting a notched surface. Sintering phenomena occurred after 2 weeks of ageing: 2W and 3W catalysts, in fact, showed a smooth surface with micro porosity in a range of about 1 μm . Backscattered images, showed in Fig. 4, revealed the presence of Pd-rich particles with dimensions less than 100 nm on 2W and 3W catalysts, evidence of coalescence of Pd species.

The experimental O_2 -TPD curves for the four catalysts are drawn in Fig. 5: as evident also from Table 1, the fresh PLZ catalyst desorbed per unit mass a number of O_2 moles higher than that of the aged catalysts, but the maximum decrease in evolved oxygen by ageing is quite small, approx. 21%. Also the peak temperature of desorption (T_p , assumed as an index of desorption mean temperature) shifted towards lower values, but always remained above 600 $^\circ\text{C}$ (temperature assumed as the limit between α - and β - O_2 species [53–55]). In Table 1 the released values of α - and β - O_2 types are distinguished: α type was practically absent in the fresh catalyst, and very limited amounts were released by the aged catalyst. Usually, the catalytic activity towards CH_4 combustion is directly linked with the amount of β - O_2 and consequently to the electro-negativity of the A- and B-site cations [56]. In the present case, the catalysts under study denoted a slightly lower β - O_2 release with ageing, but in turns its T_{50} values improved (i.e., the catalytic activity increased): Mn oxides, which emerged from the partial destruction of the initial perovskite structure, could play a key role in this case.

Comparing the TPD and TPC test results, it appeared a tight link between the O_2 desorption temperature and the catalytic activity: the lower the O_2 desorption temperature range (see the T_p values), the higher the catalytic activity towards CH_4 combustion. The trend of T_{50} (from TPC) and T_p (from O_2 TPD) were, in fact, in close agreement.

The experimental H_2 -TPR curves for the studied catalysts are drawn in Fig. 6; the calculated percentages of reducible Pd oxides (considering the PdO stoichiometry) are listed in Table 1. The PdO-reduction temperature ranges were in agreement with literature data obtained in similar conditions [11]. The PdO percentage increased upon ageing: this should be explained with the formation with ageing of Mn oxides (enlightened by both XRD analysis and FT-IR studies), which are known to increase the mobility of lattice oxygen, thus favoring the PdO phase stability [39,40]. Moreover, such increase in the PdO percentage surely contributed in maintaining a high catalytic activity towards CH_4 combustion notwithstanding the severe ageing treatment.

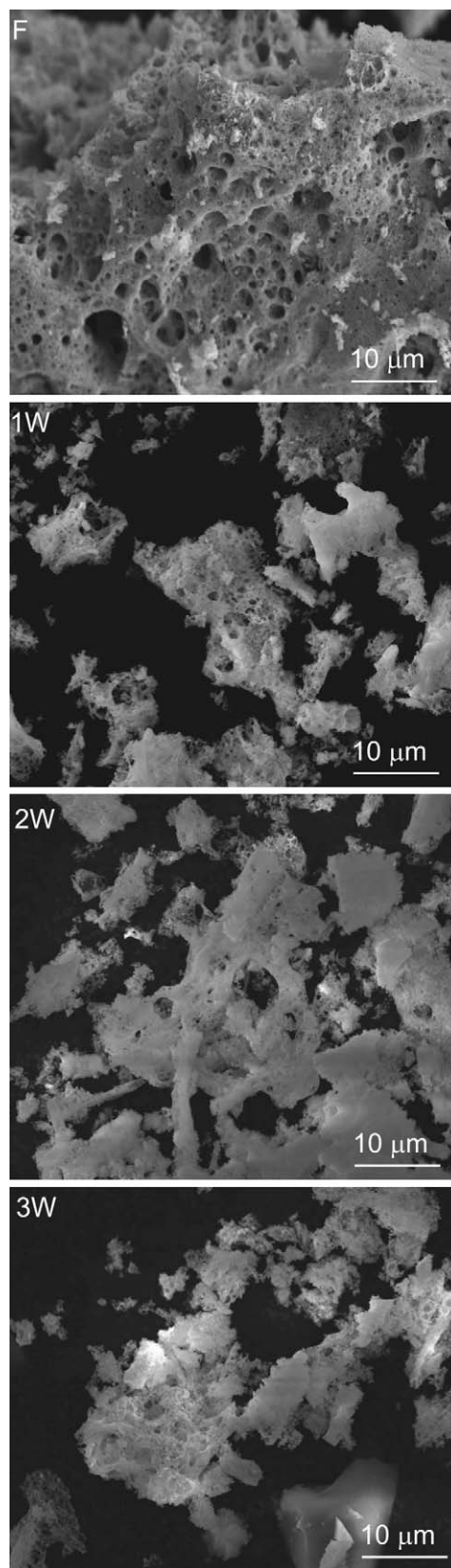


Fig. 3. SEM images of the PLZ samples under study (5000 \times).

In Fig. 7 the skeletal FT-IR spectra of the fresh and aged catalysts are reported. The fresh catalyst skeletal spectrum was characterized by a broad absorption whose intensity was increasing from 700 to 400 cm^{-1} , with a shoulder at 500 cm^{-1} , assigned to the

Table 1

Characterization of the fresh and aged samples of PLZ catalysts.

	T_{10} [°C]	T_{50} [°C]	T_{90} [°C]	BET s.s.a. [m ² g ⁻¹]	Grain size [nm]	Desorbed O ₂ (α -O ₂ ; β -O ₂) [μ mol g ⁻¹]	T_p [°C]	PdO [%]
PLZ-F	450	570	645	132.5	45 ^a ; 10 ^b	233.3 (–; 233.3)	960	29.5
PLZ-1W	500	625	690	69.5	88 ^a ; 9 ^b	205.8 (30.1; 175.7)	840; 1030	41.5
PLZ-2W	360	450	550	21.6	–	186.6 (2.5; 184.1)	860	n.d.
PLZ-3W	375	465	550	20.3	–	183.2 (2.3; 180.9)	860	78.5

^a Referred to LaMnO₃.^b Referred to ZrO₂.

metal-oxygen vibrational stretching modes in the LaMnO₃ perovskite structure [57]. Ageing led to a significant modification of the skeletal spectra: in the 2W sample spectrum three main components were detected: at 597, 500 and 418 cm⁻¹ which can be due to Mn oxides such as α -Mn₂O₃ (bixbyite) and Mn₃O₄ (hausmannite), whose spectra are also reported in Fig. 7. Mn in the aged samples was present in a reduced status. In the region 1150–1000 cm⁻¹ weak bands grew, due to ionic sulfate species.

In Fig. 8 the IR spectra of the pure powder catalyst disks after ageing and after outgassing in the IR cell are reported. It was evident from these spectra that the IR transmittance of the catalyst powders strongly diminished as a result of ageing. This was certainly related, at least in part, to the sintering of the support, as reported in Table 1, which gave rise to an increase in the grain size (as revealed by XRD) in particular for the LaMnO₃ phase, which finally increased the Rayleigh scattering of the powder [58]. In Fig. 9 the IR spectra, plotted in the absorbance scale, of fresh and 2W catalysts, both recorded at room temperature and at –140 °C, are compared. While the spectrum of fresh catalyst was essentially unchanged by lowering the recording temperature, that of 2W

catalyst was sensitive to this condition. In particular, the 2W transmittance increased (i.e., the absorbance decreased) significantly by lowering the temperature down to –140 °C; this, mostly occurring in the higher frequency range, i.e., above 2000 cm⁻¹, suggested the presence of electronic transitions, which were quenched at low temperature. This behavior, typical of semi-conducting powders, was possibly related again to the segregation of Mn oxides, or to a modification of the electronic interactions in the solid, possibly involving also Pd species.

From spectra in Figs. 8 and 9 it is also evident that the strong couple of bands centered at 1505 and 1400 cm⁻¹, with the weaker component at 850 cm⁻¹, due to stretching and deformation modes of surface carbonate species (CO₃²⁻ group [58]) disappeared already after 1 week ageing. In parallel, bands due to sulfate species were detected in aged catalyst (Fig. 10). These were a weak band at 1340 cm⁻¹, due to S=O stretching mode of a surface sulfate [57], and three strong peaks at 1130, 1031 and 973 cm⁻¹ assigned to S=O stretching vibrations of bulk or subsurface sulfate species [57], close to the frequencies of “subsurface” sulfates described for MgO-promoted LaMn_{0.5}Mg_{0.5}O₃ perovskites [59]. This effect, i.e., the disappearance of carbonate species bands following sulfatation has also been reported for NO_x storage catalysts [60,61].

In Fig. 10 the spectrum of the pure support LaMnO₃-ZrO₂ (LZ) after 2 weeks ageing is reported. It also shows the bands of sulfate species almost identical, suggesting that Pd atoms did not interact significantly with these species. No evidence can be found of PdSO₄, whose diagnostic band fell around 1430 cm⁻¹ [62]. The bands of sulfate species decreased in intensity after 3 weeks ageing, likely mostly due to sintering of the catalyst, with the corresponding decrease in the surface area.

In Fig. 11 the spectra of CO adsorbed on the pure support after activation and cooling at –140 °C are reported. The spectrum showed a main band shifting from 2166 cm⁻¹ (at high coverage) up to 2176 cm⁻¹ (low coverage). The last feature was reasonably assigned to CO interacting with Zr⁴⁺ while the position at high-loading may be associated mainly to CO on La³⁺ ions. Note that the

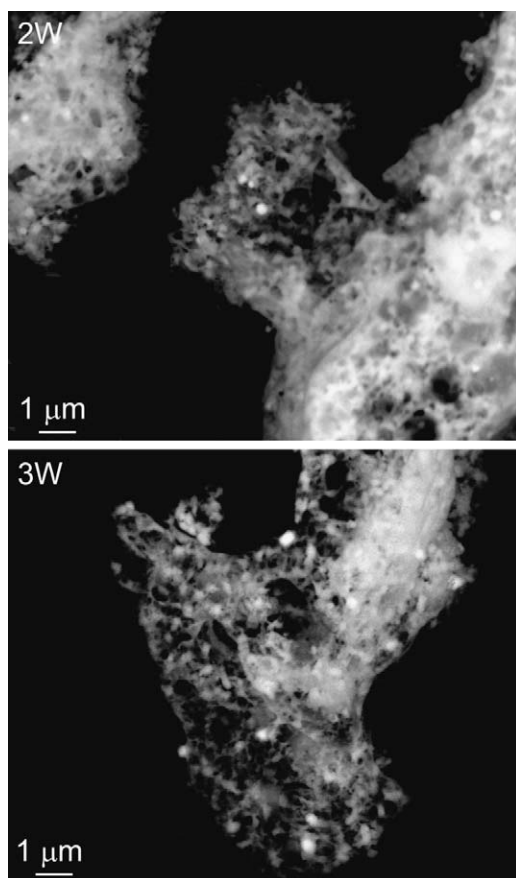


Fig. 4. Backscattered SEM images of the 2W and 3W PLZ samples under study (20,000 \times).

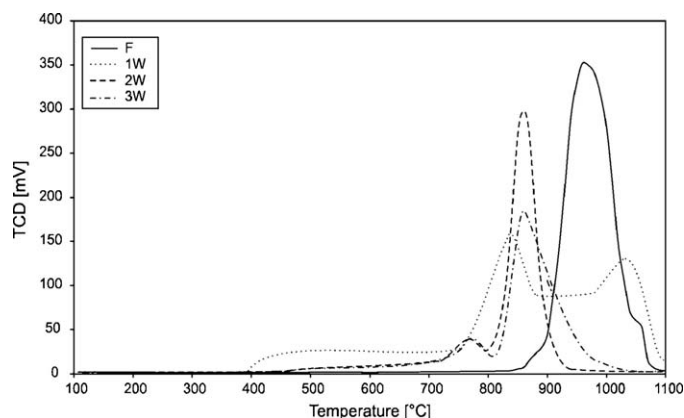


Fig. 5. O₂ Temperature Programmed Desorption (TPD) curves of the samples under study.

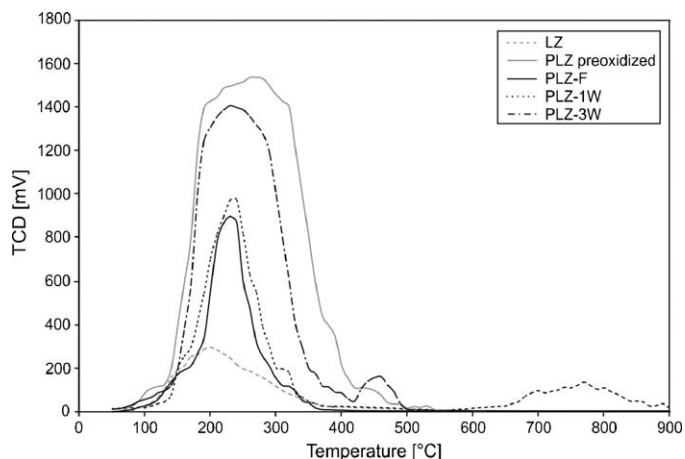


Fig. 6. H₂ Temperature Programmed Reduction (TPR) curves of the samples under study.

surface of perovskite powders ABO₃ is mostly covered by oxide anions and the larger A cations [53]. The large shift of the band was associated to the heterogeneity of the surface. The broad component at 2152 cm⁻¹, which fastly disappeared upon outgassing at low temperature, was likely due to liquid like or physisorbed CO.

CO adsorption over the fresh PLZ catalyst (Fig. 12A) gave rise to a main strong IR band whose maximum was centered at 2152 cm⁻¹ at higher loadings shifting to 2170 cm⁻¹ at the lowest loadings. The position of the maximum at low-loading was definitely different from that for the pure support. This suggested that, in this case, the main band at 2152 cm⁻¹ was predominantly due to CO interacting with cationic Pd. It is worth noting that, in our previous studies [13,17], a band at 2160 cm⁻¹ was attributed to CO on cationic Pd on Pd/CeO₂-ZrO₂ and Pd/Al₂O₃ catalysts. The subtraction spectrum reported in the inset in Fig. 12A showed that outgassing at low temperature caused the disappearance of a well-defined band centered near 2150 cm⁻¹, which however also showed a lower frequency component near 2135 cm⁻¹.

An additional weak band was evident at 2104 cm⁻¹, shifting a little bit upwards upon outgassing. This is the typical position for terminal carbonyls of zerovalent Pd. The band extended with a tail to lower frequencies, showing a distribution of different Pd metal centers [63–65]. However, bridging carbonyl species, absorbing in the region 2000–1800 cm⁻¹ and typically formed over extended Pd crystals [63–66], were not observed here. Thus, according also to the position of the band at 2104 cm⁻¹, the present spectrum was

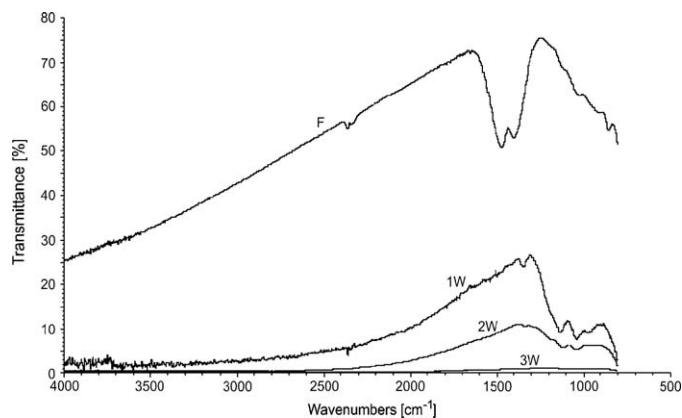


Fig. 8. FT-IR spectra (transmittance scale) of pure powder pressed disks of the F, 1W, 2W and 3W PLZ catalysts, all after outgassing in vacuum at 400 °C.

indicative of the presence of dispersed or atomic Pd metal centers, similar to those we found on Pd/CeO₂-ZrO₂ catalysts as well as on Pd/Al₂O₃ [17].

The main band of CO adsorbed on cationic centers observed on 1W definitely decreased in intensity with respect to that observed on the fresh catalyst (Fig. 12B). Additionally, its maximum on 1W catalyst, observed at a position (2167 cm⁻¹) similar to that observed on the support (2166 cm⁻¹), definitely shifted upwards with respect to the position observed on the fresh catalyst (2152 cm⁻¹). This suggested that isolated oxidized Pd centers (to which this feature was attributed above) were no more present after 1 week ageing. Additionally, also the band attributed to carbonyls of dispersed zerovalent Pd (2104 cm⁻¹) was no more evident. Almost the same result was obtained for 2W catalyst, where the presence of a broad absorption in the range 2150–2100 cm⁻¹ was even more evident (Fig. 12B, inset). These data can be discussed on the basis of our previous data obtained on Pd/CeO₂-ZrO₂ catalysts [17] and of the ones of recent surface science studies performed with innovative techniques on model “planar” catalysts [15]. According to Schalow et al. [67], as well as to Dellwig et al. [68], Pd particles grown over ordered Fe₃O₄ and Al₂O₃ substrates, respectively, were constituted by aggregates developed in (1 1 1) orientation with an azimuthal alignment with respect to the oxide support. These particles exposed (1 1 1) facets and a small fraction of (1 0 0) facets. The IR spectra of CO adsorbed over such Pd-Al₂O₃ materials [69] were actually very similar to those reported on previous studies [13,17] for CO on reduced Pd/Al₂O₃ catalysts, suggesting that the state of Pd was similar in these cases. Studies of the oxidation of Pd on these materials agree with those

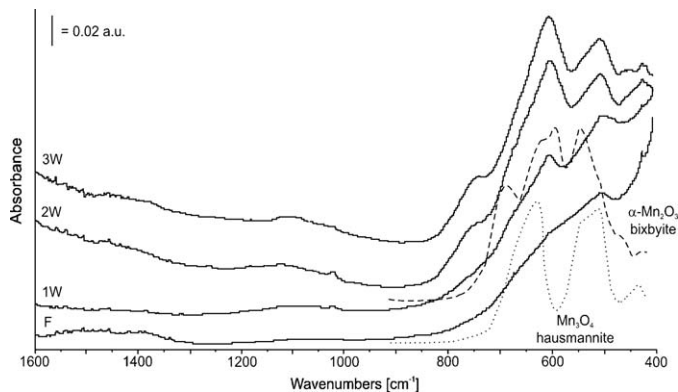


Fig. 7. FT-IR spectra of KBr pressed disks of the F, 1W, 2W and 3W PLZ catalysts, as well as of α-Mn₂O₃ (bixbyite) and Mn₃O₄ (hausmannite).

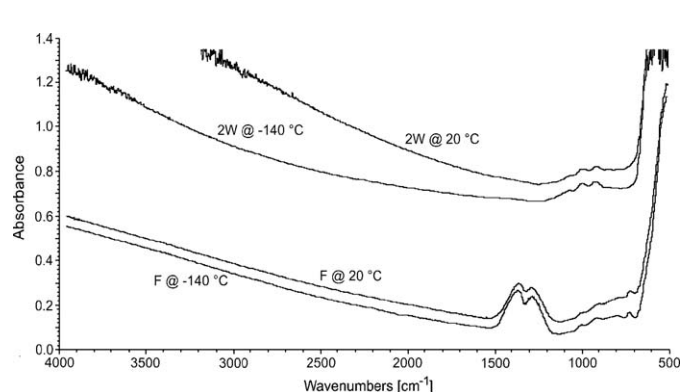


Fig. 9. FT-IR spectra of pure powder pressed disks of the F and 2W PLZ catalysts, after outgassing in vacuum at 400 °C, recorded at room temperature and at -140 °C.

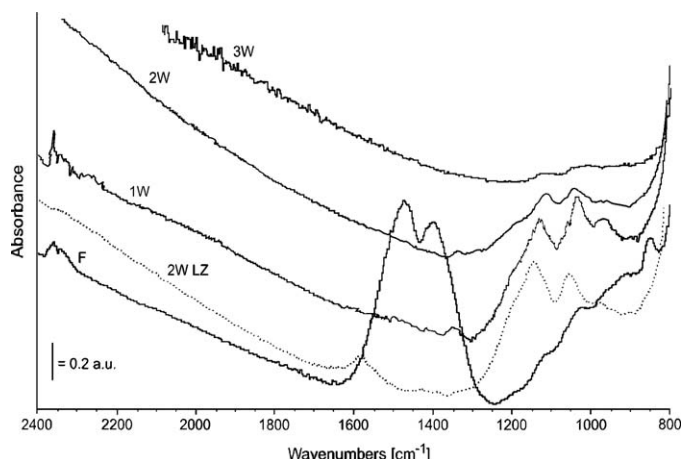


Fig. 10. FT-IR spectra (absorbance scale) of pure powder pressed disks of the F, 1W, 2W and 3W PLZ catalysts, and of the 2W LZ support, all after outgassing in vacuum at 400 °C.

reported in the literature for oxidation of Pd single crystals, as discussed by Libuda and Freund [15]. On Pd single crystal studies, it was shown that oxygen adsorbed dissociatively up to 130 °C forming ordered overlayers of chemisorbed oxygen. At higher temperatures (beyond 230 °C) the oxygen uptake was far higher and the formation of surface oxides occurred, in parallel with a major reconstruction of the Pd surface. According to Schalow et al. [69], however, two kinds of Pd oxides formed in the case of Pd/Fe₃O₄ surface. Interface Pd oxide first grew at the interface between the metal and the support; then the surface oxide growth increased by increasing the reaction temperature. These surface oxides can be dynamically formed and decomposed [69]. Pd metal surface coexisted with Pd oxide surface until 330 °C, when oxidation of the surface was complete. It seems also interesting to remark that, according to Schalow et al. [69], surface Pd oxide were not active in adsorbing CO (in their experimental conditions). Our previous data suggested that such species gave rise (in our experimental conditions) to weak and broad absorption extending from 2150 to 2100 cm⁻¹ upon low temperature CO adsorption [17]. This absorption was well evident in the spectrum in the inset of Fig. 12B, due to CO on 3W catalyst. The picture arising from these studies looked fairly the reverse of the proposal of Su et al. [70], who suggested Pd metal to form on top of its oxide.

Taking into account the present experimental results together with literature data, oxygen covered Pd metal particles formed, upon ageing, on the expense of dispersed cationic and zerovalent Pd

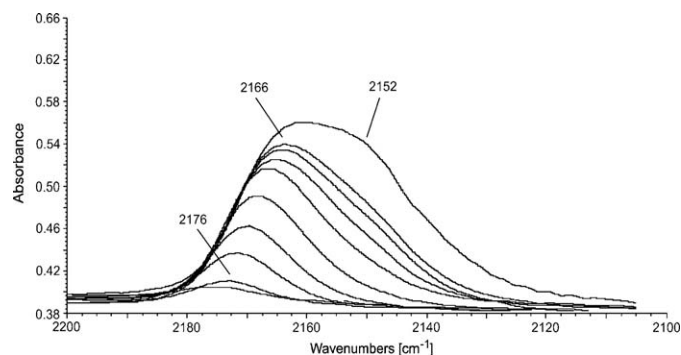


Fig. 11. FT-IR spectra of CO adsorbed on fresh LaMnO₃-ZrO₂ support (LZ), after previous outgassing at 400 °C and contact with CO 1.32 kPa at -130 °C for 5 min and successive outgassing upon progressive warming until 0 °C (from top to down). The activated surface was subtracted.

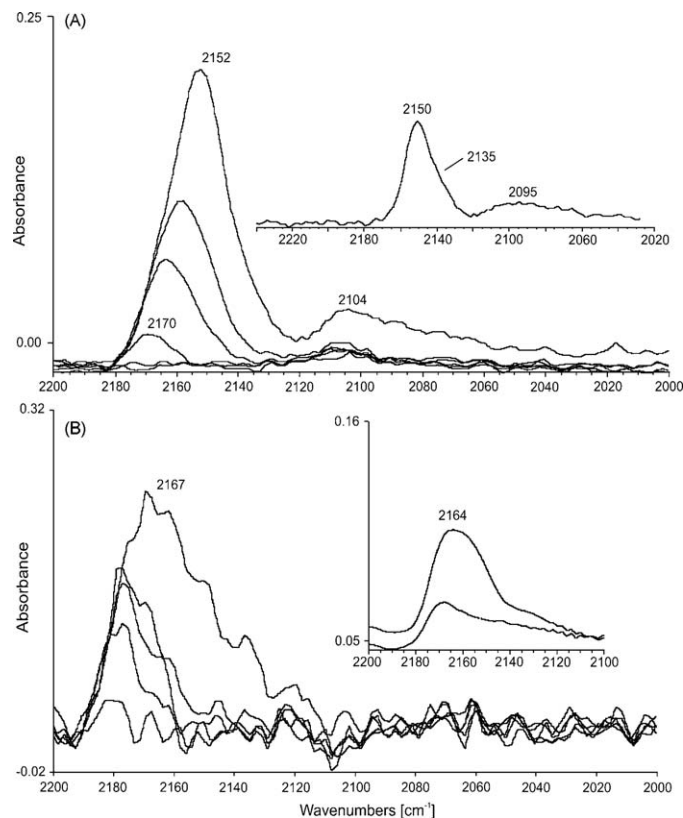


Fig. 12. FT-IR spectra of CO adsorbed (A) on sample PLZ F, after previous outgassing at 400 °C and contact with CO 1.32 kPa at -130 °C for 5 min and successive outgassing upon progressive warming until 0 °C (from top to down); in the inset: the subtraction outgassed at -130 °C—outgassed at -120 °C; (B) on sample PLZ 1W, after previous outgassing at 400 °C and contact with CO 1.32 kPa at -130 °C for 5 min and successive outgassing upon progressive warming until 0 °C (from top to down). In the inset: FT-IR spectra of CO adsorbed on sample PLZ 2W, after previous outgassing at 400 °C and contact with CO 1.32 kPa at -130 °C for 5 min and successive outgassing at -70 °C. The activated surface was subtracted.

atoms, which were predominant on the fresh catalyst. Such oxygen covered Pd metal particles were detectable only by a very careful analysis of the IR spectra of low temperature adsorbed CO, being responsible of a weak and broad absorption extending from 2150 to 2100 cm⁻¹. However, the catalyst retained and even increased, in the present case, its low temperature catalytic activity in CH₄ oxidation. It seemed likely that the definite increase in the catalytic activity of the catalyst upon ageing was associated to the phase modification occurring in the bulk support, where Mn oxides segregated. It is likely that oxygen covered Pd metal particles on Mn rich oxides were more active than when they interacted with other catalytic materials, less or not active themselves in catalytic oxidation.

4. Discussion

The present study showed that PLZ catalysts are active catalysts in CH₄ oxidation, although their performances are lower than those of Pd/CeO₂-ZrO₂ studied previously with the same techniques [17]. In both cases, highly dispersed Pd cationic and metal centers, were predominant on the fresh catalysts. These species, that may work synergistically, are certainly active in low temperature CH₄ oxidation. It seems that Pd dispersed on CeO₂-ZrO₂, where both CeO₂ and ZrO₂ are found [17], is more active than those dispersed on LaMnO₃-ZrO₂, at whose surface likely predominates. In any case, this suggests that the most usual interpretation of the activity

of supported Pd oxidation catalysts, as closely related to Pd/PdO equilibrium, is a simplification possibly valid only for highly loaded catalysts.

This work also showed the unusual behavior of PLZ, whose catalytic activity at low temperature increased upon ageing in the presence of SO₂-containing gas. Upon this treatment, surface carbonates, well evident on the fresh catalyst, were substituted by surface and bulk sulfates. The obtained data were in agreement with the phenomena observed by Alifanti et al. [52]. These authors proposed that an irreversible formation of sulfate species at the surface of LaCeMnCoO perovskite catalysts was initiated around the transition metal cation responsible for the oxidation activity and accumulated around the La³⁺ ions. This behavior, however, was thought to be not very relevant with respect to the evolution of the catalyst activity.

A likely more relevant phenomenon observed here upon ageing, was the segregation of Mn oxides, which went in parallel with the conversion of highly dispersed Pd metal and Pd oxide species into oxide covered small Pd metal particles. As a consequence, the catalytic activity at low temperature increased very much becoming higher than that of aged Pd/CeO₂-ZrO₂, which was found to be much more active in the fresh state [17]. The Mn oxides, well known in literature for their good catalytic activity towards CH₄ combustion [39], could be probably responsible of the enhanced catalytic activity of PLZ with ageing.

Highly dispersed Pd centers, predominant on fresh catalysts, tended to convert into oxygen covered Pd metal particles, which were also active species in low temperature CH₄ oxidation. These species were responsible for very weak and broad absorption in the range 2150–2100 cm⁻¹, found in all the tested catalysts, upon low temperature CO adsorption. The weakness of the adsorption of CO and of its vibrational perturbation was likely due to the small polarizing power of Pd²⁺ ions and also by their low Lewis acidity, associated to the strong basicity of the oxide ions in PdOx species.

5. Conclusions

The catalytic activity and long-term stability of 2% Pd/LaMnO₃-ZrO₂ catalysts for natural gas combustion was deeply investigated. The catalyst, prepared via solution combustion synthesis, was completely characterized in the fresh status, and in the aged one, after prolonged treatment under hydro-thermal ageing and S-compounds poisoning. An increased catalytic activity towards NG combustion with ageing was detected. Highly dispersed Pd centers were predominant on fresh catalyst. Upon ageing, oxygen covered Pd metal particles formed, at the expense of dispersed cationic and zerovalent Pd atoms. The increase in the catalytic activity of the sample upon ageing was associated to the phase modification occurring in the bulk support, where Mn oxides segregated. The Mn oxides are, in fact, well known in literature for their good catalytic activity towards CH₄ combustion. Moreover, bands due to sulfate species were detected in aged samples: IR analysis showed that Pd atoms did not interact significantly with these species. The bands of sulfate species decreased in intensity after 3 weeks ageing, likely mostly due to sintering of the catalyst, with the corresponding decrease in the surface area.

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